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THE ROLE OF THE EPOXY RESIN: CURING AGENT RATIO IN COMPOSITE INTERFACIAL STRENGTH BY SINGLE FIBRE MICROBOND TEST

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ABSTRACT

This paper focuses on an investigation into the role of the epoxy resin: curing agent ratio in composite interfacial shear strength of glass fibre composites. The procedure involved changing the percentage of curing agent (Triethylenetetramine [TETA]) used in the mixture with several different percentages used, ranging from 4% up to 30%, including the stoichiometric ratio. It was found by using the microbond test, that there may exist a relationship between the epoxy resin to curing agent ratio and the level of adhesion between the reinforcing fibre and the polymer matrix of the composite.

1 INTRODUCTION

This investigation took place since although the interface between the fibre and matrix of a fibre-reinforced composite has been highly researched over the past two decades, there are still clear gaps in understanding regarding what the effect of the size, curing agent and epoxy agent used may have on the interfacial properties of the composite. With composites now increasingly being used in a wider range of industries in greater quantities, the need to produce composites which are able to endure harsher climates and working environments has never been higher.

In order to maximise the mechanical performance of the composite material it is critical to optimize the stress transfer capability of this interfacial region. This is important since if there is a poor level of adhesion between the fibres and the polymer matrix within the composite then it cannot reach its true potential maximum strength. An accepted mechanically measured value for the strength of this property is the interfacial shear strength (IFSS) which can be influenced by chemicals, for example silane coupling agents [1]. This has led to several investigations [2,3] revolving around how the IFSS varies within both glass fibre and carbon fibre-reinforced composites using the microbond test.

In particular, the topic of how the epoxy resin to curing agent ratio affects the adhesion between the fibre and the matrix has not been particularly well documented (if at all) for glass fibre-reinforced composites. It is generally accepted that the interfacial adhesion properties of a glass fibre-reinforced composite are maximised when the ratio of epoxy resin to curing agent is set at or around the stoichiometric ratio, due to the nature of the chemistry promoting the maximum level of bonding and thus strength. However this has never been thoroughly investigated using the microbond test. Hence this investigation focussed on monitoring if varying the epoxy resin to curing agent ratio altered the

adhesion properties in any manner and whether any links could be drawn to other areas of research.

2 EXPERIMENTAL

2.1 Materials

The experiments were carried out using boron free E-glass fibres, sized with Aminopropylsilane (APS), taken from larger roving's manufactured by Owens Corning. The epoxy resin used was Araldite 506® and the curing agent used was Triethylenetetramine (TETA) with a technical grade of 60%. Both were produced by Sigma Aldrich.

2.2 Sample Preparation

The procedure of preparing the samples was conducted in a checklist manner, with the same procedures being carried out for each experimental batch in the same order to as much the same timescale as possible. Each batch contained 60 samples in order to receive enough data for statistical parity. The preparation began with applying the APS sized glass fibres to sections of 20mm gauge length card through the use of double sided tape before then applying Loctite® super glue. Great care was taken to ensure that the fibres were protected from as much contamination or damage as possible during the handling process. After one day, once the glue had set, the samples for testing were prepared by applying tiny levels of the epoxy resin: curing agent mixture onto the APS sized glass fibres as micro-droplets. This mixture was prepared by calculating the weight (mg) necessary for both the epoxy resin and curing agent respectively to meet a predefined percentage, for example the stoichiometric ratio (around 14.2 parts TETA per 100 epoxy or $\approx 12.3\%$). This mixture was then thoroughly mixed before being degassed for 15 minutes using a composite vacuum pump to increase the level of homogeneity within the mixture.

Once vacuumed, the mixture was again stirred before being applied to the fibres with as little time delay as possible. The time between the finishing of the vacuuming and the application to the fibres was very important since the mixture could begin to cure to some small degree as soon as it was exposed to air at room temperature. The fact that the reaction within the mixture was an exothermic reaction potentially would not help matters since this would provide an extra degree of heat which could speed up the curing process. However the level of negative defects this reaction might introduce within the resulting micro-droplets is as yet unknown.

The application process involved applying several droplets to each fibre. It proved difficult to produce only one single droplet on a fibre however the extra droplets allowed for the most suitable one in terms of size, shape and condition to be chosen for testing. In some cases it was possible to test two droplets on the one fibre, providing a direct comparison. The application of the droplets was completed using a modified scalpel [4], which had a piece of thin steel wire attached to the end of the blade, creating a precise tool. This allowed for the end of the wire to be dipped into the mixture, transferring several droplets onto its surface before then being applied to the glass fibre by gently touching the wire against the fibre. The position/orientation of the fibre during this procedure varies from lab to lab but in this case the fibres were suspended horizontally during the procedure. The gauge length of the fibres was maintained at 20mm throughout the experiment.

Once all micro-droplets were applied, the fibres were placed in an oven for curing. A consistent program was used throughout the study, with the first step of the heating program taking the temperature within the furnace up to 60°C at a rate of 2°C/minute whereupon this temperature was maintained for one hour. The temperature was then ramped up again at a rate of 2°C/minute before it reached 120°C whereupon this was maintained for two hours, resulting in a total time of three hours, 50 minutes spent in the furnace (not including cool down time).

Once the samples had been cured and had cooled then the following step was for them to have a number of dimensions measured using an optical microscope. The optical microscope allowed for

samples to be viewed under high magnification and photographed, allowing for the measurement of the fibre diameter (D_f), droplet diameter (D_d) and embedded length (L_e) to be calculated. These measurements were required if the IFSS was to be correctly calculated by using the microbond test since the embedded area of the droplet needs to be known [5,6] as shown in Equation 1 where F_{max} is the maximum load applied to the droplet before it de-bonds.

$$\tau = \frac{F_{max}}{\pi \cdot D_f \cdot L_e} \quad (1)$$

2.3 Microbond Test

The effect of altering the epoxy resin: curing agent on the adhesion properties of the composite was investigated through the use of the microbond test. The microbond test is generally accepted as a universal test for measuring the important adhesion properties at work between the fibre and the polymer matrix. An example of such a property is the interfacial shear strength (IFSS) which details the ability of the interface of the composite to deal with any shear stress placed upon it [7].

The microbond test apparatus can involve several different methods for clamping the specimen in a manner that the glass fibre can pass freely through but the micro-droplet cannot and will thus at some point de-bond from the fibre. Such methods again vary from lab to lab but for this particular setup an Instron tensile test machine was used with a specially designed rig [4][6]. This rig made use of two sharp blades which were extended out until they grasped the micro-droplet, with said droplet positioned underneath the blades. Particular care had to be taken to ensure that the blades were not over tightened since this could result in the fibre being partially damaged or entirely severed in some cases. The movement of the blades was also adjustable, with multiple screws being designed into the rig to allow for the motion of the blades to be sped up or down as required [4]. Care had to be taken since damage could be done to the blades themselves if they were to over tightened, which would result in them colliding into each other.

Once the sample was in place, and the details inputted into the Instron computer program, the tensile machine would begin to gradually pull the fibre upward at a rate defined by the user. In this case the rate for these experiments was maintained at a constant value of 0.1 mm/s throughout. Thus the micro-droplet would gradually be pulled upwards into the two blades and begin to deform against them. This deformation would continue till a critical point was reached where the droplet would lose adhesion with the fibre and de-bond, breaking its connection with the fibre and slipping down the fibre or in some cases completely off the fibre, leaving tell-tale signs of where the droplet had once been in the form of a meniscus. The graph of a successful de-bonding is provided is Figure 1.

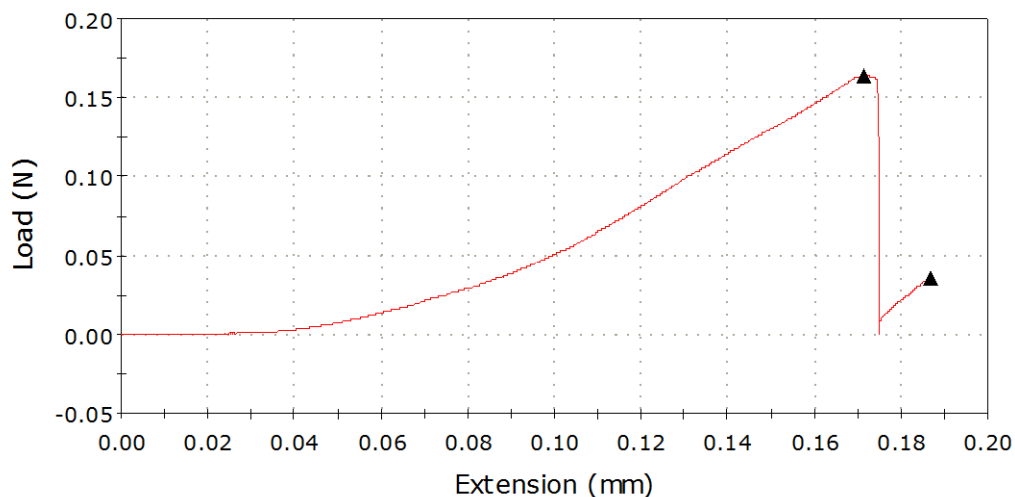


Figure 1: Graph Successful De-bond as shown on Instron

3 RESULTS

Once each sample had been successfully tested, the data was removed from the Instron machine and examined in numerical and graphical form using Microsoft Excel. Typically the data recorded by the Instron included the maximum load (mN), the calculated embedded area ($1000\mu\text{m}^2$), the calculated IFSS (MPa), the tensile stress at maximum load in the fibre (MPa) and the tensile strain at maximum load in the fibre (mm/mm).

The data which was of primary interest were the values for maximum load recorded for each droplet combined with the calculated embedded area producing a maximum load against embedded area. Figure 2 presents a typical peak load against embedded area graph constructed from microbond results [1].

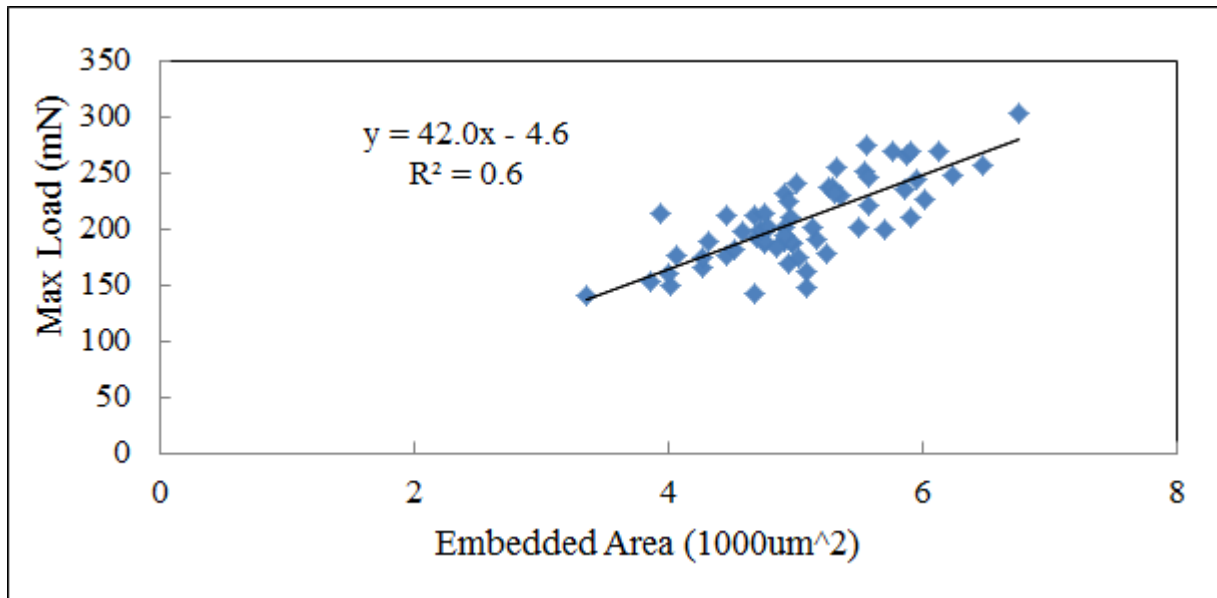


Figure 2: Max Load vs Embedded Area for 22.5%wt TETA

When the average values for the IFSS were taken from each batch and plotted, it was observed that as the ratio was altered the average IFSS value varied, reaching a maximum value around the stoichiometric value. After this maximum value, the values of average IFSS began to decrease although with a much gentler slope than that before the peak value. This resulted in an inverted parabola shape for the results as shown in Figure 3.

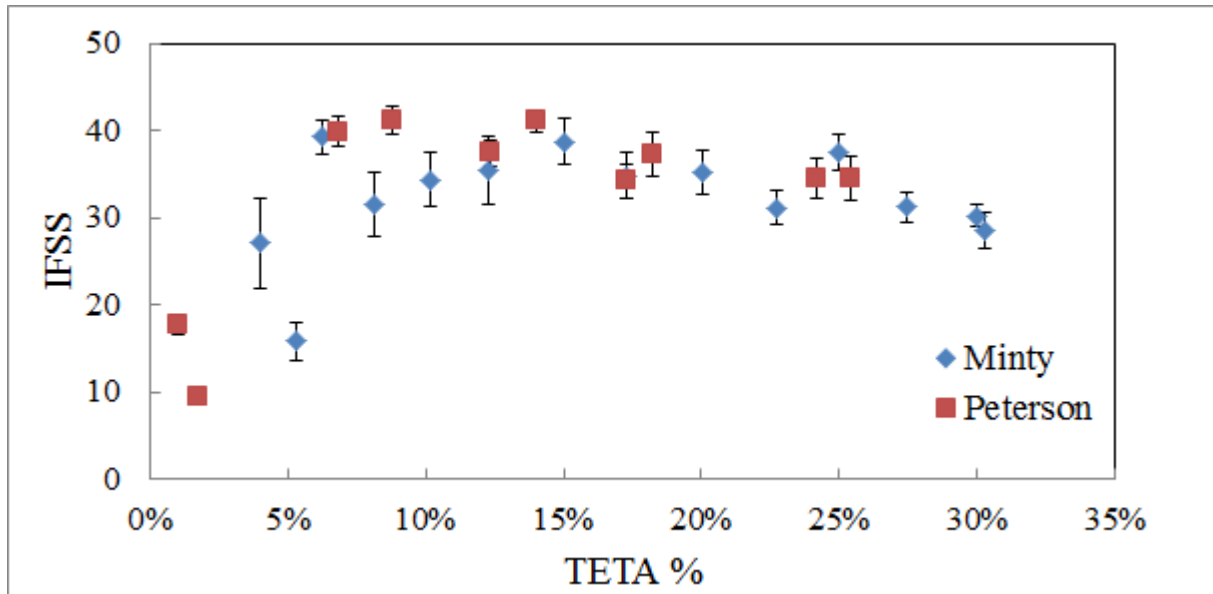


Figure 3: Graph of IFSS vs TETA % wt in Polymer matrix

4 DISCUSSION

In many cases it was found that the application of the force to the micro-droplets might not have been entirely uniform. This meant that the samples would not necessarily de-bond uniformly, instead de-bonding in a manner that left portions of the droplet on the fibre where it had been originally located. These remnants varied in size but typically were much larger than the standard degree of residue which would be left from a clean de-bonding. It was postulated that this may have led to the large degree of scatter within the results taken as detailed in Figure 3. It was found that by re-examining the micro-droplets underneath the optical microscope it was for most cases possible to measure the remaining residue and re-calculate corrected values for the embedded area. With this taken into account, this led to a general increase in the IFSS values calculated and led to the scatter being decreased to some degree. Furthermore this procedure could potentially be further enhanced by examining the tested samples using a Scanning Electron Microscope (SEM). This would give an even more accurate picture of the corrected embedded length and how much residue was left on the fibre after a successful de-bonding.

In more extreme cases the fibre would twist considerably as the forces were applied which would lead to the fibre breaking just as the micro-droplet de-bonded during some tests. As can be imagined, this was frustrating since although the data could have been acceptable it would now be impossible to inspect the method of de-bonding underneath an optical microscope or SEM, hence not allowing for the calculation of a corrected embedded area. This scenario coupled with the nature of some of the droplets de-bonding suggested that there may have been inconsistencies within the microbond rig, primarily the respective height of each of the blades. If the blades of the rig were not exactly in line with each other, this could lead to the force not being applied equally across the surface of the droplet, resulting in the fibre twisting or the droplet breaking in two, rather than de-bonding as a whole. However due to that nature of the rigs design, it was accepted that it can be incredibly difficult to enable the blades to line-up exactly 100% of the time, thus this had to be covered for in the level of error defined acceptable in the microbond test experiment, with a strict procedure now in place to prevent this from happening.

Another difficulty encountered was in producing uniform, axi-symmetric micro-droplets on the glass fibre. In many cases several droplets were not entirely axi-symmetrical which could lead add to the non-uniform force application mentioned previously. It was found that as the ratio of the epoxy

resin: curing agent varied further from the stoichiometric value (whether above or below) it became progressively harder to produce the ideal micro-droplets required for testing.

5 CONCLUSIONS

Clearly there does exist a relationship between the epoxy resin to curing agent ratio and the level of adhesion between the reinforcing fibre and the polymer matrix, with results seeming to identify that peak performance is gained around the stoichiometric ratio. Since interfacial adhesion is widely accepted as being critical to composite performance it is an obvious requirement that further research be conducted.

One potential explanation could be the interaction between the epoxy resin to curing agent mixture and the APS size present on the glass fibre. Sizes are introduced to bare glass fibres to enhance their adhesion properties as well as protect the fibres from damage from water among other things. A considerable level of research has been done in the role of sizes in the adhesion properties and yet there is still a degree of unknown in exactly what level of effect they have on composite performance – specifically, why they improve the adhesion properties (currently it may be accepted that they simply work and it is, as yet, not fully understood why [1]).

As such it seems acceptable to perhaps postulate that the interaction between the size and the epoxy resin to curing agent is altering the adhesion properties, and as such the performance of the composite. Thus it could be beneficial to test glass fibres which have been sized with different sizes instead of APS to see if this theory could be both confirmed and applied to other sizes currently used within the industry. Other lines of research could be in researching if the purity of the curing agent plays a key role in this interaction or if the curing taking place before the samples are placed in the oven clearly changes how the micro-droplets perform during testing. Both would fill gaps that currently exist within the current knowledge base.

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